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ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

VOLUME 6

**Emulsion Polymerization
to
Fibers, Manufacture**

A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

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DAVID L. BEACH
Chevron Chemical Co.

YURY V. KISSIN
Mobil Chemical Co.

ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE

Ultrahigh molecular weight polyethylene (UHMWPE) is a high density polyethylene with a molecular weight over 3×10^6 . Chemically, high density polyethylene (HDPE) and UHMWPE are identical; both are straight-chain linear polymers. The molecular weight of conventional HDPE is rarely above 50,000, whereas ASTM definitions require a molecular weight of UHMWPE above 3×10^6 ; it can be as high as 6×10^6 (ASTM D 4020). Crystallinity of UHMWPE is typically about 45%.

The long molecular chain of UHMWPE confers the following unique combination of properties (see Table 1): abrasion resistance greater than that of any other thermoplastic; the highest impact toughness of any plastic, even at cryogenic temperatures; good corrosion resistance and excellent environmental stress-crack resistance; resistance to cyclical fatigue; noise- and shock-abatement properties; low coefficient of surface friction; nonstick surface; and resistance to radiation. In addition, UHMWPE has been approved by the FDA, USDA, and National Bureau of Standards sanctions for pure water and food handling.

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Table 1

Property
density,
Vicat soft
hardness
Rockwell
durometer
deflection
tensile prop-
erty
ultimate
yield strength
elongation
elongation at
double-strand
abrasion
mean coefficient
expansion
-30 to
0 to
30 to
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Table 1. Properties of HIMONT 1900 Ultrahigh Molecular Weight Polyethylene

Property	Value	Test method
density, g/cm ³	0.93	ASTM D 742
Vicat softening point, °C	135	ASTM D 1525B
hardness		
Rockwell, R scale	52	ASTM D 785
durometer, D/15	67	ASTM D 2240
deflection temperature at 445 kPa ^a , °C	75	ASTM D 648
tensile properties		ASTM D 638
ultimate strength, MPa ^b	40.7	
yield strength, MPa ^b	20	
elongation at yield, %	4	
elongation at break, %	300	
double-notched Izod, J/m ^c	0.37	HIMONT P116
abrasion index	10	HIMONT P159
mean coefficient of linear thermal expansion, per °C		ASTM D 696
-30 to 0°C	1.3×10^{-4}	
0 to 30°C	1.3×10^{-4}	
30 to 60°C	2×10^{-4}	
coefficient of friction ^d at 23°C		
static	0.20-0.25	
dynamic	0.15-0.20	

^a To convert kPa to psi, multiply by 0.145.^b To convert MPa to psi, multiply by 145.^c To convert J/m to ft-lbf/in., divide by 53.38.^d Against chromium-plated steel.

The polymerization process for UHMWPE employs a Ziegler catalyst similar to that for conventional HDPE. The process can be batch or continuous. Most UHMWPE is produced by a slurry process, but both solution or bulk processes are applicable. The polymer is supplied as a fine powder that can be ram extruded or compression molded. Most of the production is converted into semifinished sheets, plates, bars, rods, tubes, and extruded profiles. Industrial parts are made by machining the semifinished stock. Some parts are made directly by compression molding or forging.

Formulation

Unlike other thermoplastics, UHMWPE can be thermally processed without additives or stabilizers because the long polar chains are resistant to scission, and even when broken can have a mol wt > 10⁶. However, fillers and modifiers are used. Graphite fibers, powdered metals, and glass fibers and beads improve stiffness, decrease deformation under load, and increase heat-deflection temperatures. Because of superior properties, UHMWPE can compete with rigid engineering plastics (qv). Except for graphite and glass fibers, most additives lower abrasion resistance and impact strength (see Table 2).

Peroxide cross-linking (qv) enhances abrasion resistance and reduces deformation under load but affects impact strength and stiffness. Typical properties of cross-linked UHMWPE are given in Table 3. Alloying improves temperature

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Table 2. Properties of Filled Ultrahigh Molecular Weight Polyethylene^a

Resin composition	Abrasion index, % ^b	Heat-deflection temperature, °C ^c	Impact strength, J/m ^d
unfilled	13-15	70-80	1335-1708
filler, phr			
mica ^e , 5	23	73	320
mica ^e , 20	15	85	53
calcium carbonate, 5	23	80	1228
calcium carbonate, 20	19	78	427
talc ^f , 5	24	70	53
talc ^f , 20	16	87	
silicon dioxide ^g , 1	15	74	1441

^a 1900 UHMWPE, $[\eta] = 20$ dL/g, $\bar{M}_w = 3.2 \times 10^6$.^b % Volumetric loss of test material in a sand-water slurry abrasion test compared to the volumetric loss of a C-1018 steel control piece with the same dimensions.^c At 455 kPa (66 psi).^d Double-notched Izod impact test at 23°C. To convert J/m to ft-lb/in., divide by 53.38.^e Alsibronz #12 (mica).^f Talc (Vansil 3371).^g Fumed SiO₂, Silanox 101, Cabot Corp.Table 3. Properties of Cross-linked 1900 UHMWPE^a

Property	Cross-linking agent, phr					Test method
	0	0.2 ^b	0.5 ^b	0.2 ^c	0.5 ^c	
abrasion index ^d , %	13-15	7	9	6	6	HIMONT PTC-159
compressive deformation at 13.8 MPa ^e at 50°C after 24 h, %	12	7	7	6	11	ASTM D 621
heat-deflection temperature at 455 kPa, °C	70-80	64	56	74	58	ASTM D 648
double-notched Izod impact at 23°C, J/m ^f	0.46-0.59	0.41	0.37	0.39	0.26	HIMONT PTC-116
Rockwell hardness R scale	50-60	50	22	45	44	ASTM D 785
density, g/cm ³	0.935	0.927	0.925	0.927	0.924	ASTM D 792

^a Average mol wt = 3.2×10^6 .^b Lupersol 101, Pennwalt Corp.^c Vul-Cup R, Hercules Inc.^d Value represents the percent volumetric loss compared to a C-1018 steel with the same dimensions when tested in a 50:50 sand:water slurry medium.^e To convert MPa to psi, multiply by 145.^f To convert J/m to ft-lbf/in., divide by 53.38.

resistance without significant loss of impact or abrasion resistance. Silicone oils and molybdenum disulfide reduce the already low coefficient of friction even further.

Processing

Because of its extremely high molecular weight, UHMW resin cannot be readily processed by thermoplastic melt-processing techniques such as injection molding (qv), blow molding (qv), thermoforming (qv), or screw extrusion (qv). The long-chain molecules do not melt or flow like other thermoplastic resins. For

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example, (130°C) do indicating can be pro ram extru such as ge Both tion-mold minor ma cost part- A me sheet. The to minimi tained for

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example, a block of UHMWPE heated well above the crystalline melting point (130°C) does not change in shape, but only in appearance from opaque to clear, indicating the disappearance of crystal structure. Nevertheless, UHMW resin can be processed by compression molding into sheet, block, and precision parts; ram extrusion into board, rods, pipe, and profiles; and forging into complex parts such as gears, wheels, sprockets, and cams.

Both HIMONT U.S.A., Inc., and Hoechst in the FRG are developing injection-molding techniques for UHMWPE, with modified molding conditions and minor machine modifications. Because of progress made in these programs, low cost part-molding techniques should be available in the near future.

A modified metal-stamping process is employed to form parts from UHMWPE sheet. The sheet is heated to 149°C (ca 20°C above its crystalline melting point to minimize springback) and is placed in the stamping die. Die pressure is maintained for a short time to allow the sheet to cool before removal.

Applications

The principal applications of UHMWPE are in chemical processing, the food and beverage industries, foundries, the lumber industry, bulk materials handling, medical implants, mining, mineral processing, paper, recreational equipment, textiles, and transportation. In Italy and the United States, UHMWPE is used for highly efficient battery separators. A recent application is in very strong, light fibers made by gel spinning.

Railcar manufacturers and maintenance engineers are using UHMWPE as a permanent solid lubricant to protect metal surfaces. Automobile assembly lines are using UHMW polymer parts to reduce energy costs, noise, and maintenance costs.

Liners made of UHMWPE permit lightweight aluminum bulk trucks and trailers to haul sharp or abrasive cargo.

Hoppers lined with UHMWPE have reduced the unloading time of freighters because UHMWPE is slippery and wear resistant. In the coal and electric utility industries, chutes, hoppers, bins, and conveyor rollers are lined with UHMWPE to prevent wet or frozen fines from sticking.

In farm machinery, the replacement of heavy cast-iron sprockets, idlers, wear plates, and wear shoes with UHMWPE parts saves weight, reduces lubrication, and lowers fabrication and maintenance costs. Automated foundries use UHMWPE liners to mix, convey, and store binder sand, which sticks to most other surfaces.

The life of sewage-treatment plants is extended significantly and energy costs are reduced by replacing cast-iron wear shoes, bearings, and sprockets with UHMWPE parts.

In lumbering, UHMWPE is used for chute, sluice, and chain-drag liners. In sawmills, metal contact surfaces are replaced with UHMWPE to facilitate sliding without lubricant or rust staining.

Radiation resistance of UHMWPE is better than that of other thermoplastic and thermoset resins. It is also an effective neutron shield. As with other plastics, excessive doses eventually cause embrittlement; however, the threshold is high. See also RADIATION-RESISTANT POLYMERS.

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The use of UHMWPE in food processing and handling is covered by FDA Regulation 21CFR177-1520 and USDA acceptance for meat, poultry, and food processing. The absence of additives permits application in pure water systems and in prostheses and other medical devices.

At present, UHMWPE is produced in the United States by HIMONT U.S.A., Inc. (1900) and American Hoechst (Hostalen Gur), in Japan by Ashai (Sunfine-U), and in the FRG at a bulk price of \$1.98/kg. Worldwide capacity is 27,000-34,000 metric tons; worldwide consumption is about 22,650 t.

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J. J. COUGHLAN
D. P. HUG
HIMONT U.S.A., Incorporated

MODIFIED POLYETHYLENES

- Chlorinated polyethylene, 495
Chlorosulfonated polyethylene, 513

Because of its chemical nature, polyethylene is relatively inert to most chemical reagents. Its structure and reactivity are similar to those of normal and branched hydrocarbons. However, reactions that proceed to only a very limited extent with alkanes may produce large effects on the properties of polyethylene.

As discussed in earlier sections of this article, polyethylene varies widely depending on the method of production, which determines linearity and density. The products of modifying reactions of polyethylene vary according to both the degree of crystallinity of the starting polymer and its microstructure, as well as to the extent of modification.

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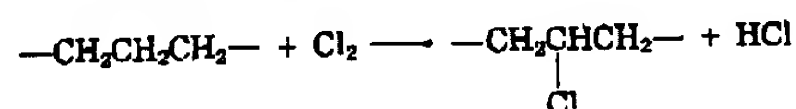
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Chlorinated Polyethylene

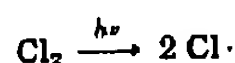
Of the many chemical reactions used to modify polyethylene, chlorination and chlorosulfonation are the most important commercial methods. The properties of chlorinated polyethylene (CPE) depend on the properties of the starting material and on the amount and distribution of the chlorine introduced.

Chemistry of Preparation

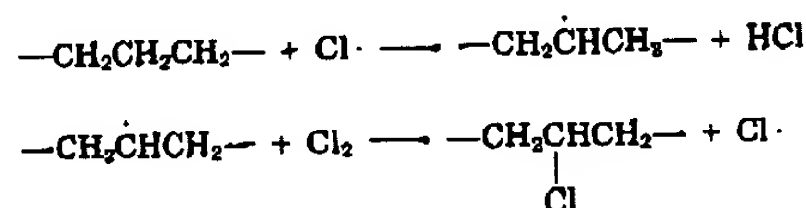
In the chlorination of polyethylene, a chlorine atom is substituted for a hydrogen atom on the polymer chain, accompanied by the formation of HCl:



This occurs by a free-radical mechanism, usually catalyzed by ultraviolet light or initiators:



The chlorine radical abstracts a hydrogen atom from the polymer chain, leaving a carbon radical, which reacts with a molecule of chlorine to attach one chlorine atom to the polymer chain and liberate the other to continue the chain reaction:



The overall chemistry is independent of the medium, although significant differences in the specific kinetics and mechanism may occur.

If the polymer is crystalline, chlorination begins at amorphous areas and crystalline surfaces, followed by melting and exposure of fresh areas for chlorination. Thus, the crystallinity of the polymer is gradually destroyed. If the entire chlorination process is carried out in a heterogeneous system (no solvation) at low temperature, traces of crystallinity persist far above 50% chlorine content. A plot of percent chlorine versus average number of chlorine atoms per ethylene unit (2 carbon atoms) is shown in Figure 1. Zero chlorine atoms per unit represent polyethylene, whereas one chlorine atom per unit represents the same average chlorine content as poly(vinyl chloride) (PVC), 56.7%.

It is clear that chlorine must be concentrated in certain regions of the polymer to permit polyethylene crystals to survive when the polymer contains as much chlorine as PVC. This uneven distribution is referred to as block chlorination.

Chlorination in solution (1–4), on the other hand, tends to be more uniform, being limited only by solvation, ie, how well the chains are "stretched out." In this situation, crystallization of the polymer may be prevented by a chlorine

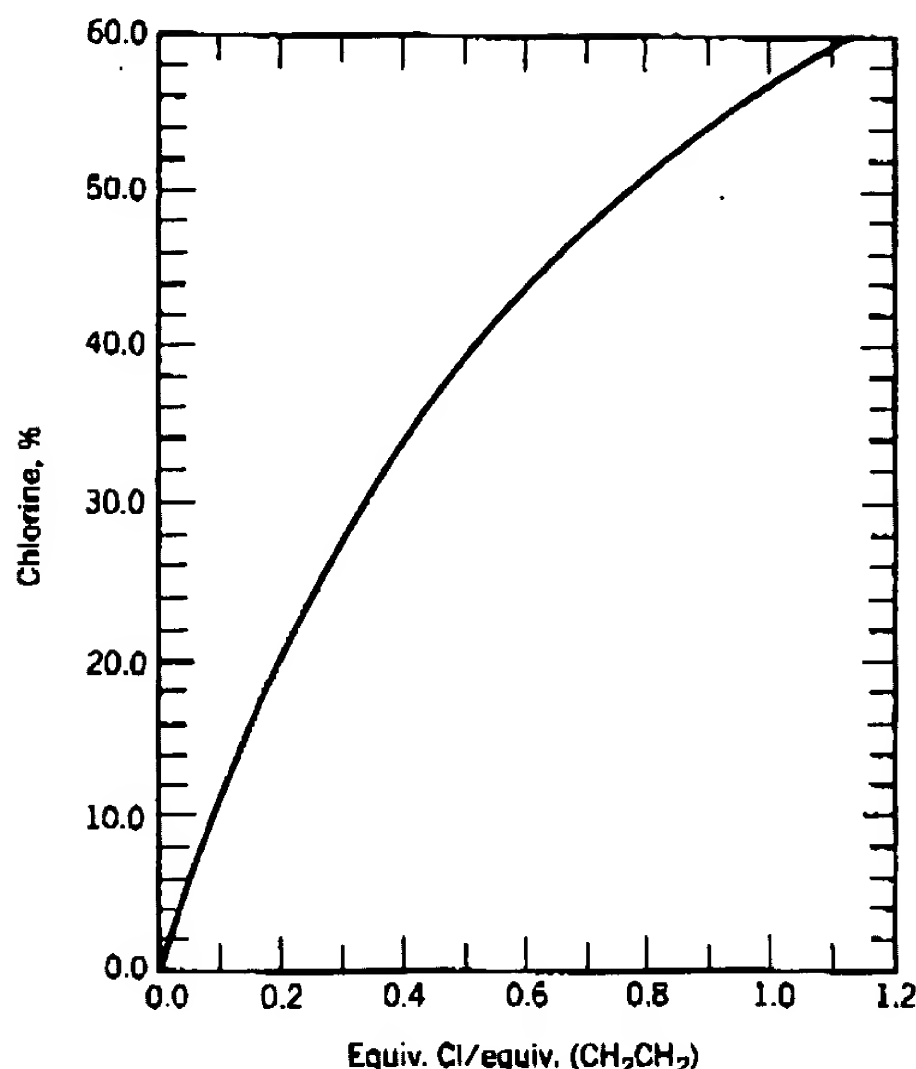


Fig. 1. Chlorine atoms per ethylene unit vs % chlorine content of chlorinated polyethylene.

content less than 30%. Chlorination in the absence of physical barriers is called a random process.

Block chlorination occurs at low temperatures with the polyethylene particles suspended in a liquid or gaseous medium, eg, a fluidized bed. If the polyethylene becomes amorphous because of increasing temperature, chlorination occurs throughout, but access to some areas (depending upon internal structure and particle shape and size) may be hindered. The result is not truly random and is referred to as hindered chlorination.

The morphology of the polymer and accessibility of the polymer chains to the chlorination determine the chlorine distribution and therefore the properties of the polymer produced.

In practice, chlorination occurs by a combination of all processes. In industry, solvents are used as little as possible because of the problems associated with the recovery and disposal of chlorinated solvents. Controlled hindered chlorination processes avoid the use of solvents and can give products with the desirable properties produced by random chlorination. The chlorine distribution in CPE produced by various processes has been studied by nmr (5-10).

In most chlorination processes, 1 mol HCl is generated for 1 mol of chlorine added to the polymer. Much of the cost of producing CPE is associated with the removal, recovery, and disposal or utilization of this hydrogen chloride. These problems can be avoided by employing chlorine oxide (Cl₂O) as the chlorinating agent (11).

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Chlorination Processes

Solution (Solvent) Processes. Very low density polymers may dissolve at temperatures as low as 60°C, but high density polymers may require a temperature of 110°C or higher for dissolution (1-4). At ambient temperature, the polymer remains crystalline, and block chlorination occurs.

Chlorinated methanes or ethanes are typically preferred; complete dissolution of the polymer may generate appreciable vapor pressures. The total pressure (vapor plus gases) may be reduced by temperature control during the process.

The molecular weight of the polymer and the resulting viscosity can be critical in a solvent process. Difficulty in isolating the polymer in a finely divided form and solvent recovery are disadvantages of this process.

Processes Without Solvent. Aqueous Suspension. The most widely used commercial process for CPE employs an aqueous suspension (12-16). Temperature control is excellent with reasonably high reaction rates. The reaction exotherm and the heat of dissolution of the HCl formed reduce the expenditure of energy in this hindered chlorination process. Temperatures near or above the crystalline melting point of the polyethylene are required at some stage to produce an amorphous polymer. Because of the low solubility of the chlorine in the aqueous phase, an overpressure of chlorine is required.

The reaction medium is highly corrosive, and washing and drying the product require large amounts of water and energy. Since the polymer is not solvated, the slurry viscosity is independent of the molecular weight. The starting polymer, however, must be in suitable particle form; this may require grinding.

Anhydrous Processes. Particle form processes (17-20) typically require agitation in a fluid-bed, rotary-blade, or rotary-kiln reactor; the heterogeneous process makes temperature control difficult. Nevertheless, such processes are attractive because drying of the product is eliminated, and the HCl produced can be separated from the gas stream in anhydrous, marketable form.

Melt processes (21) involve chlorination of the molten polymer, with constant exposure of fresh surfaces by shearing and mixing.

Anhydrous processes appear to produce slightly more block chlorination and more color problems than aqueous processes.

Other Processes. Various combinations of the above processes can be used to produce CPE (22-25). In virtually all cases, block chlorination is controlled by the reduction of the polyethylene to a form that is amorphous or of low crystallinity at some stage during the chlorination process.

Properties

The hardness (qv) of CPE varies widely (26,27). Commercial products are soft, with a chlorine content of 23-48%. The tensile properties of flexible CPE polymers are often compared to those of flexible PVC, but the stress-strain characteristics are different (see also VINYL CHLORIDE POLYMERS). The contrast between the unmodified CPE and the flexible PVC is marked, as shown in Figure 2 (28). Although the two samples have similar Shore A hardness values, because of the similarity of slope of their stress-strain curves near the point of origin,

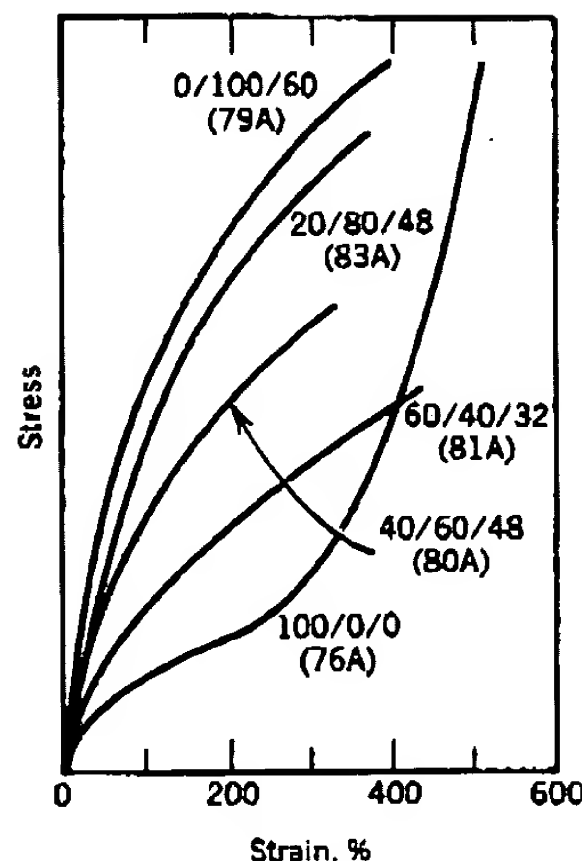


Fig. 2. Stress-strain curves for combinations of CPE (42% Cl)/PVC/plasticizer Santicizer 711; Shore hardness A given in parentheses (28). Monsanto Santicizer 711 is a phthalate ester of mixed linear alcohols with 7-11 carbon atoms.

the 100% modulus value of the CPE is much lower than that of the PVC. The stress of the CPE sample increases slowly until the strain exceeds 300%. Very soft CPE samples may show a slight yield at about 100% elongation. Thus, an amorphous CPE sample is typically more easily deformed than a PVC sample of comparable hardness. Furthermore, the CPE elongates much more before breaking. As might be expected from the stress-strain curves, soft amorphous CPE polymers in the thermoplastic state exhibit poor creep resistance. However, they can have excellent elongation and impact resistance (qv) at low temperatures, as shown in Figure 3 (6) for a low crystallinity polymer containing 36% Cl. Flexibility of a CPE polymer is compared with a flexible vinyl or other polymer by employing Shore A hardness (ASTM D 2240) with an instantaneous (1 s) reading to minimize creep effects or a Tinius Olsen stiffness tester (ASTM D 1043) (see also POLYMER CREEP).

Effect of Chlorine Content. Chlorine distribution can greatly affect the properties of CPE polymers, which are otherwise identical. The common CPE polymers, however, have chlorine distributions that are at least partially random.

Applying the 100% modulus (unit stress at 100% elongation) of a CPE as a relative measure of flexibility within the family produced from a given PE, maximum softness is obtained with 35-40% chlorine. A 100% modulus of less than 1.4 MPa (200 psi) (Shore A ca 75) can typically be obtained with 26-50% chlorine, but above 50% the minimum modulus attainable rises rapidly. Maximum elongation at break typically occurs with 28-35% chlorine, with the maximum attainable value beginning to fall before 40% chlorine is reached. A 500-800% or greater elongation at break is expected for most unmodified polymers.

Low Temperature Properties. CPE undergoes a sharp transition at about -20°C , which is often referred to as its glass-transition temperature but is more

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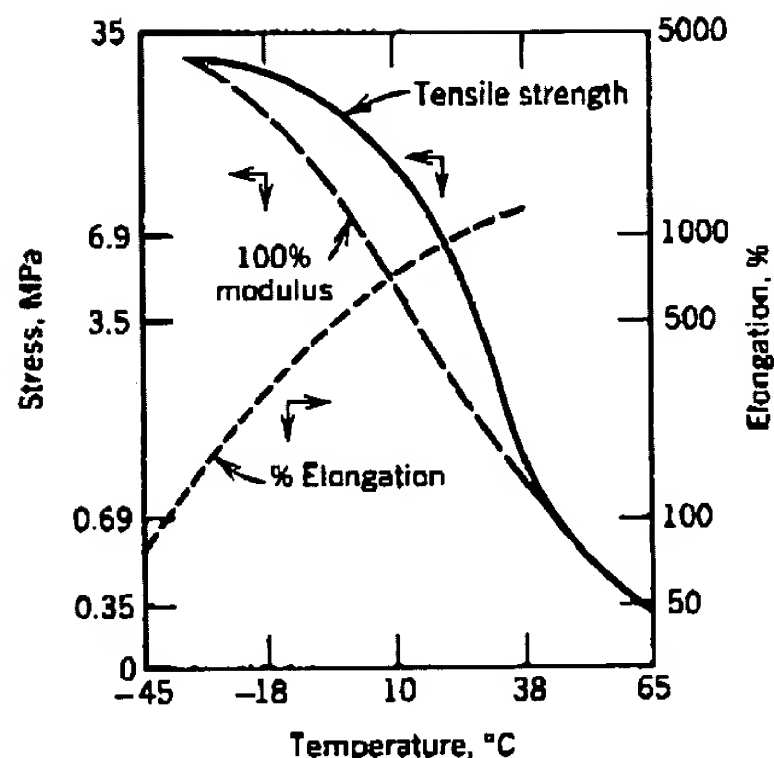


Fig. 3. Properties of CPE (36% Cl) vs temperature. To convert MPa to psi, multiply by 145.

like a beta-type transition (29). Stiffening is significant at this transition, with retention of ductility and impact resistance.

The actual brittle point as measured by ASTM tests is more likely to be in the range of -40 to -70°C , depending upon the content and distribution of Cl and the presence of additives. As the chlorine content exceeds about 30–35%, the transition temperature gradually rises. At a chlorine content of 48–50%, this transition is more likely to occur around 10°C , with a correspondingly higher brittle point.

The variation of the modulus of rigidity (ASTM D 1043) with temperature of CPE and flexible PVC is shown in Figure 4 (30). The CPE stiffens more rapidly than the phthalate-plasticized vinyl as the temperature drops, but it does not become as stiff. The greater ductility of the CPE at lower temperatures makes it more resistant to brittle failure.

Solubility. At chlorine contents of 42% and above, amorphous CPE polymers are quite soluble in polar and aromatic hydrocarbon solvents. They dissolve with shear mixing without heat and form viscous solutions containing as little as 8–10% solids, depending upon molecular weight. Typical solvents include toluene, chlorinated methanes and ethanes, ketones (but not acetone), chlorinated aromatics, and other polar solvents (31,32). The resistance of CPE to aliphatic hydrocarbons is generally rated as good because it is not very soluble and does not rely on an extractable plasticizer for flexibility.

Chemical Resistance. CPE polymers are little affected by aqueous solutions of most salts, even at elevated temperatures. Oxidizing acids, eg, nitric acid, and their salts, however, can degrade CPE. Amines and ammonia react with CPE. Aqueous solutions of phosphoric and sulfuric acid, up to about 50%, have little action, but more concentrated sulfuric acid can cause severe swelling. Some solvents, eg, tetrahydrofuran, cause swelling by absorption even from a dilute water solution.

Prolonged exposure of CPE film to distilled water at elevated temperatures

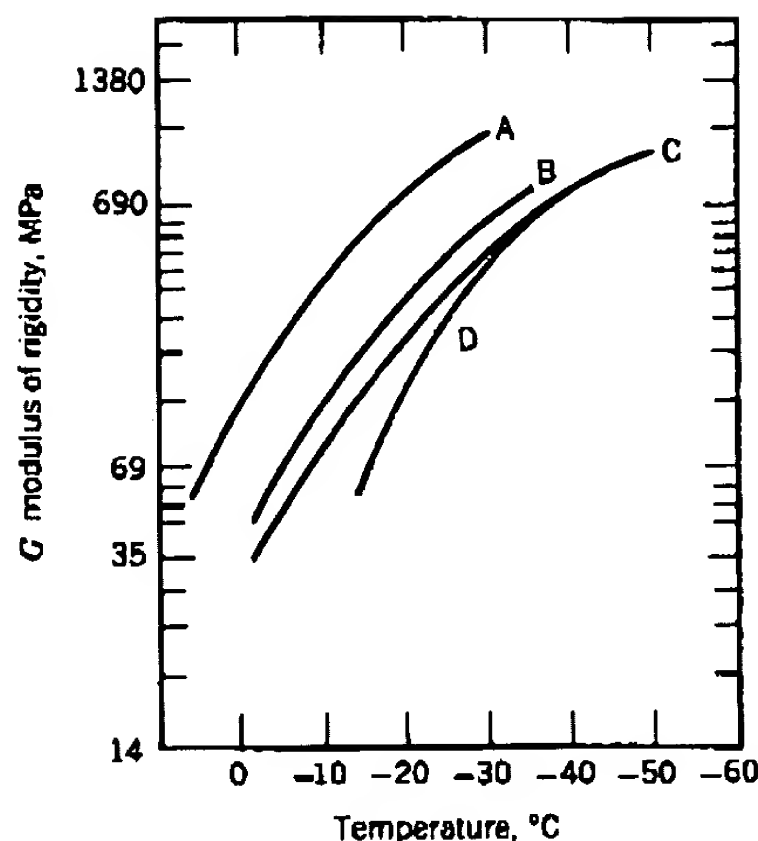


Fig. 4. Low temperature flexibility (ASTM D 1043). A, PVC (K-63) plus 70 phr polymeric plasticizer; B, 75% CPE (42% Cl) resin, 25% PVC; C, PVC plus 57 phr dioctyl phthalate; D, CPE (36% Cl) resin. Formulation = Dow CPE resin, 100 phr; Ba-Cd stabilizer, 2.0 phr; epoxidized soybean oil, 3.0 phr; phosphite chelator, 0.5 phr; and lubricant, 1.0 phr. To convert MPa to psi, multiply by 145.

may cause considerable swelling because of osmotic effects. Many CPE polymers, prepared by chlorination in aqueous suspension, contain ionic impurities. On prolonged warming in distilled water, a film of such a CPE can show a reversible weight increase of 40% or more. This problem is avoided by using water of zero hardness in manufacturing and washing, or by using additives and fillers.

Dielectric Properties. The dielectric constant of CPE tends to increase with increasing chlorine content, reaching a maximum in the 30–45% range, then decreases (30,33,34). Higher current frequency tends to give a peak in dielectric constant at a lower chlorine content.

Viscosity. The viscosity of a CPE polymer increases with chlorine content and with the molecular weight of the parent PE. The rheology curves of several CPE polymers are compared in Figure 5 (30) with those of a rigid PVC, a plasticized PVC, and a high density polyethylene (HDPE) with a melt index (MI) of 0.8. The flow characteristics of CPE polymers resemble those of low molecular weight PVC resins, ie, they exhibit a very high viscosity at low shear rates; thus, attempts to measure the melt index are of no value. These polymers exhibit good flow at higher shear rates.

Permeability. In general, chlorination first increases the gas permeability of polyethylene by disrupting the crystal structure. Depending upon the gas in question and the chlorine distribution, permeability usually reaches a maximum at a chlorine content between 10 and 35%, then decreases. Vapors from CPE solvents may show a different behavior. The permeability of a CPE film containing 45% Cl resembles that of rigid PVC more than that of flexible PVC. The permeabilities of CPE to water vapor and oxygen are shown in Figures 6 and 7, respectively (26).

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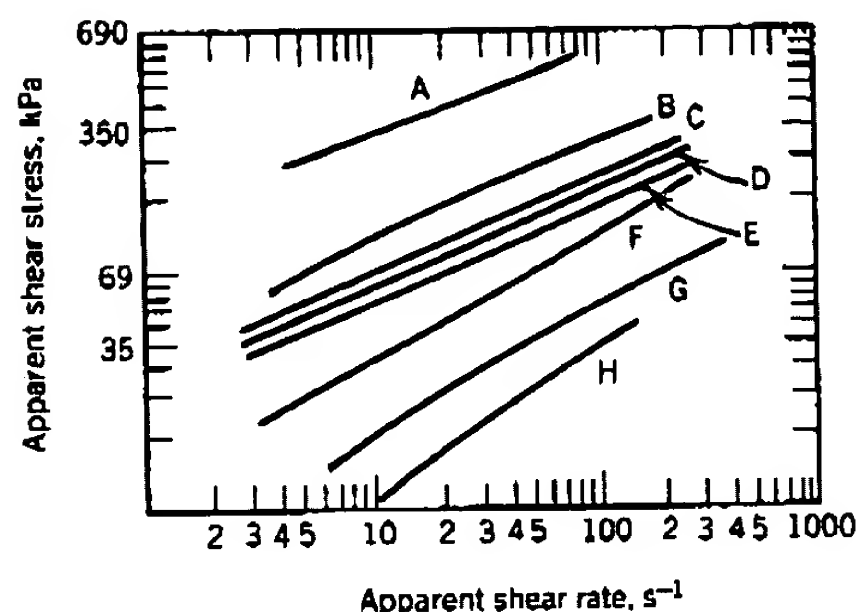


Fig. 5. Rheology curves; shear rate determined in 12×50 -mm capillary at 190°C . A, Pipe grade PVC; B, CPE (36% Cl) 12% PVC/24% plasticizer; C, CPE (42% Cl) 12% PVC/18% plasticizer; D, CPE (36% Cl) 18% PVC/15% plasticizer; E, CPE (25% Cl) 20% PVC/14% plasticizer; F, PE; G, PVC + 50 parts DOP; and H, PVC + 80 parts DOP. Formulation = Dow CPE resin, 100 phr; Ba-Cd stabilizer, 2.0 phr; epoxidized soybean oil, 3.0 phr; phosphite chelator, 0.5 phr; and lubricant, 1.0 phr. DOP = dioctyl phthalate; to convert kPa to psi, multiply by 0.145.

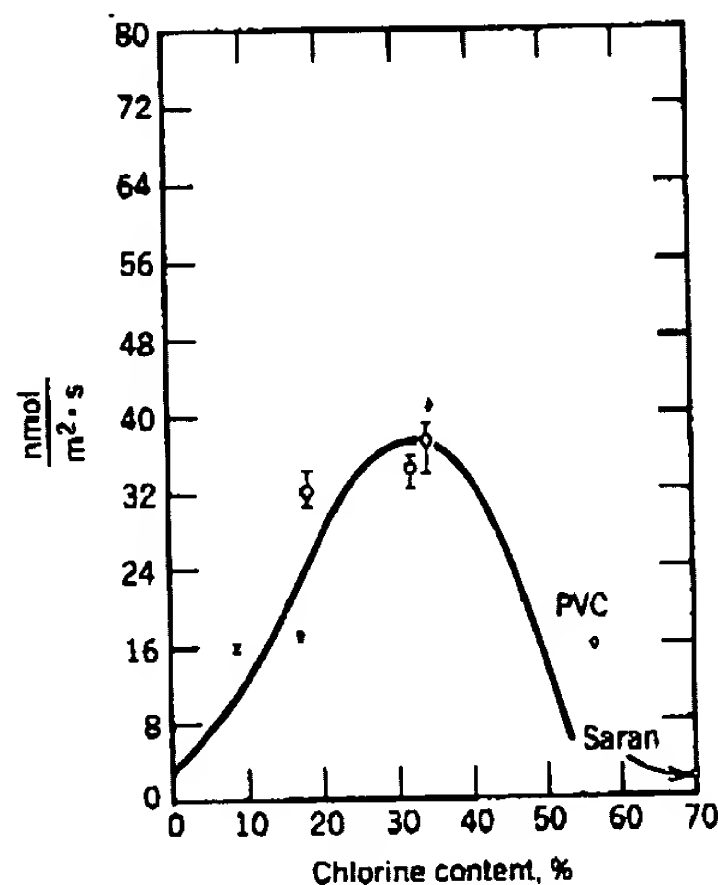


Fig. 6. Water-vapor transmission rate as a function of chlorine content of chlorinated polyethylene. To convert $\frac{\text{nmol}}{\text{m}^2 \cdot \text{s}}$ to $\frac{\text{g} \cdot \text{mil}}{100 \text{ in}^2 \cdot \text{d}}$, divide by 8.

Burning Characteristics. The chlorine in CPE confers resistance to ignition, which can be greatly increased by the addition of flame-retardant (FR) synergists. The effect of additives on the limiting oxygen index (LOI) (ASTM D 2863) is shown in Table 1. Because CPE does not flow well at low shear rates, it usually chars rather than drips when burning. In the absence of fillers, it generates large quantities of fine ash. Adding CPE to a polymer compound promotes

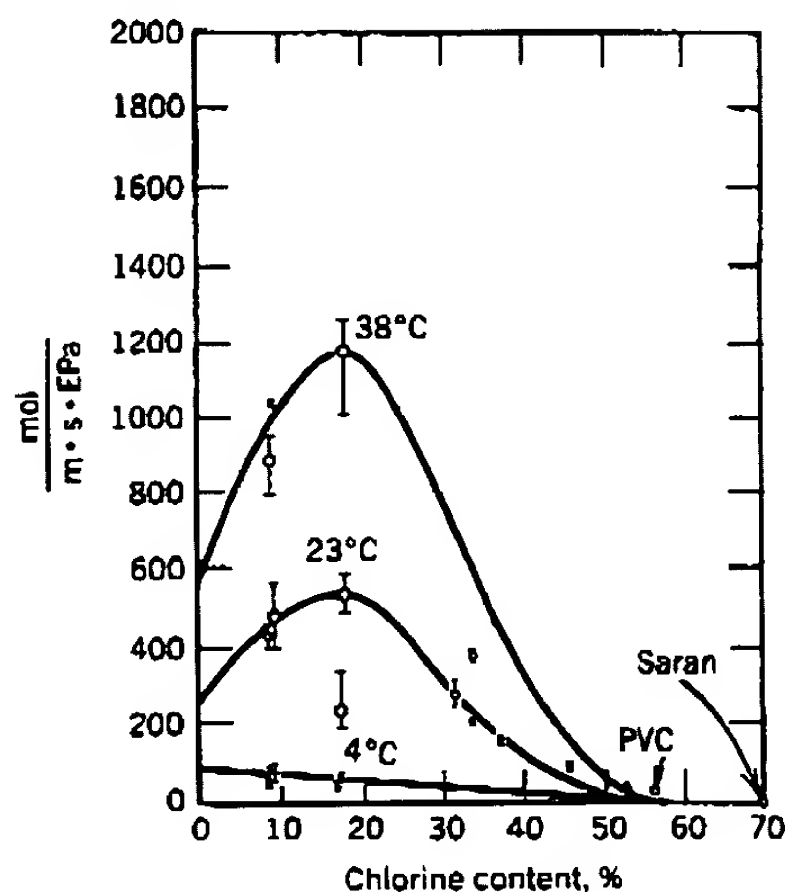


Fig. 7. Oxygen permeability as a function of chlorine content of chlorinated polyethylene. To convert $\frac{\text{mol}}{\text{m}^2 \cdot \text{s} \cdot \text{EPa}}$ to $\frac{\text{cm}^3 \cdot \text{mil}}{100 \text{ in.}^2 \cdot \text{d} \cdot \text{atm}}$, multiply by 0.5.

Table 1. Effect of Flame-retardant Synergists on the Limiting Oxygen Index^a of a CPE Compound

Synergist ^b added, 5 phr	Change in LOI, % O ₂ ^c
Firebrake ZB	+4.5
tricresyl phosphate	-2.5
triphenyl phosphate	-2
tetrabromophthalic anhydride	+3.5
hexabromobenzene	+3
antimony oxide	+6
Firebrake ZB + tetrabromophthalic anhydride	+8.5

^a The LOI of a 42% chlorine PE is 25% O₂.

^b These ingredients are evaluated here to demonstrate synergism as measured by the LOI test and not as a recommendation.

^c ASTM D 2863. Small-scale tests are useful in comparing behavior of different materials but do not indicate behavior in a fire.

the tendency to char when the material burns; therefore, CPE should not be added to an FR compound in which dripping is part of the extinguishing mechanism.

Effect of Chlorine Distribution. A CPE polymer exhibiting a very small heat of fusion can be produced with the addition of less than 25% Cl in hindered chlorination. Block chlorination may give a product of measurable heat of fusion with a chlorine content above 57%.

The effect of the first 5–8% chlorine is probably independent of the process,

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but as chlorination proceeds differences become dramatic. A block chlorination product typically exhibits maximum flexibility between 10 and 20% chlorine, with stiffness increasing rapidly thereafter and the polymer becoming glassy and brittle at ambient temperature with a chlorine content as low as 30%. Increasing the degree of block chlorination, eg, in a hindered chlorination process, is associated with an increase in the glass-transition temperature.

With block distribution of chlorine, an increase in the apparent melt viscosity can be expected. Block chlorination gives polymers less soluble and more oil and solvent resistant than random chlorination does.

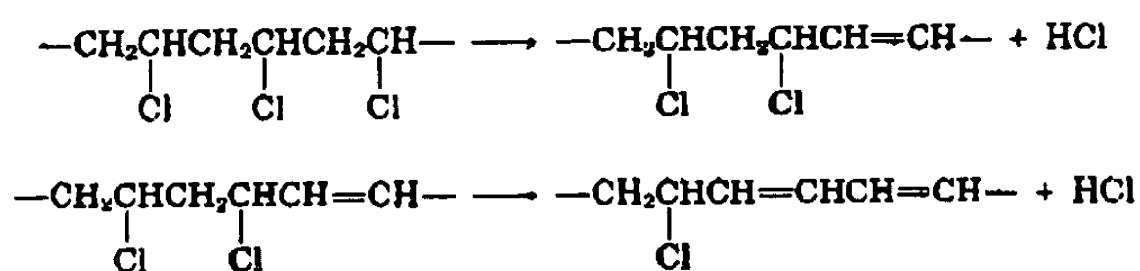
If controlled block chlorination is allowed with retention of a functional degree of crystallinity and the chlorine content is kept below 30%, a thermoplastic elastomer (TPE) is obtained. The resinous portion consists of polyethylene crystals, whereas the amorphous regions are those that have been chlorinated. With a higher chlorine content, eg, 42%, the product is stiff and very viscous with a high glass-transition temperature (see also ELASTOMERS, THERMOPLASTIC).

Effect of Parent Polyethylene. Higher molecular weight polyethylene yields a CPE with higher viscosity and tensile strength. A polyethylene with a narrow molecular weight distribution yields, for a given melt index, a CPE with a higher viscosity and lower shear sensitivity than does a PE with a broad molecular weight distribution and the same melt index. Residual crystallinity from a high density polyethylene yields a CPE with a better heat-deformation resistance than obtained with comparable crystallinity in a parent low density polyethylene (LDPE). Lower molecular weight CPE polymers have lower solution viscosities.

Compounding

Thermoplastic Compositions

Stabilizers. Like vinyl compounds, CPE is protected with heat stabilizers during processing. Possessing fewer chlorine atoms that are more irregularly placed than in PVC, CPE does not undergo "zipper" degradation like PVC, wherein every loss of HCl produces a reactive allylic (boldface below) chlorine:



Tin or other stabilizers, designed to block this "unzippering" of PVC, usually do not stabilize CPE. Initially, CPE appears to lose HCl in a random fashion, catalyzed by the HCl generated (35-37). The heat stability of CPE is enhanced by acid acceptors, even by alkaline substances capable of initiating the breakdown of PVC. Typical acceptors include epoxidized soybean oils, cycloaliphatic epoxy compounds, magnesium oxide, and metallic carbonates. Additives containing zinc or iron should be used with care because these metals can catalyze decomposition of CPE compounds.

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A barium-sodium complex organophosphate (38) is an extremely effective heat stabilizer for CPE, and CPE-PVC blends combined with a tin mercaptide. Tin maleates, combined with this complex organophosphate, are excellent stabilizers for CPE-styrene polymer blends.

Lead stabilizers work reasonably well in CPE-PVC blends, but mixed metals are often required, such as barium-lead, calcium-tin, barium-tin, barium-cadmium, and barium-cadmium-zinc (low zinc). Cadmium usually creates problems with color. For example, a sample lightly pigmented in white shows a pinkish tinge after oven aging at 80°C for 72 h or more (pinkings). Solid barium-cadmium stabilizers sometimes "bloom" or "plate out," especially in styrene blends. In some CPE compositions, a simple combination of calcium stearate (1-2 phr) with epoxidized soybean oil (2-4 phr) may suffice, especially for laboratory evaluation; a liquid barium phosphite chelate can also be used. Typical concentrations of heat stabilizers range from 1.5 to 4 phr, with 2-7 phr of epoxidized soybean oil as an auxiliary stabilizer.

Antioxidants. Antioxidants (qv) are used in CPE compositions to improve performance. They are needed for processing only with very hot melt mixes (200-230°C). If color stability is being studied with accelerated heat aging or dynamic stability testing, the use of an antioxidant is advisable, such as a hindered phenol at 0.1-0.5 phr. Elastomer antioxidants, such as hindered amines, are frequently used in black materials exposed to sunlight.

Lubricants. Higher concentrations of lubricants are used in CPE compositions because of greater compatibility. A combination effective for extrusion and calendaring is 0.7-1.5 phr stearic acid with 1-1.5 phr PE wax or oxidized PE wax; 2-5 phr of LDPE may also be added to improve surface characteristics.

Plasticizers. CPE appears to be compatible with plasticizers (qv) of lower polarity, eg, chlorinated paraffins or long-chain phthalates, and with polymeric plasticizers. The CPE polymers, being flexible, usually require less plasticizer than PVC. Heat aging of plasticized CPE can be excellent (39). When it is combined with plasticized PVC, the degree of hardness of the resulting compound may be unexpected (28). A high plasticizer content can cause surface tack.

Fillers and Pigments. CPE is compatible with fillers and shows an elastomeric reinforcement response to carbon blacks at concentrations of 5-20 phr (see also CARBON). Reinforcing fillers increase viscosity, sometimes excessively. Nonreinforcing fillers, such as calcium carbonates, can be used generously, with improved melt homogeneity and flow. Excessive amounts of filler impair tensile strength and elongation. Fillers (qv) may affect low temperature properties.

Pigments containing traces of free zinc or iron may impair heat stability. Pigments sensitive to pH require a buffer. For outdoor exposure, black compounds are best formulated for long-term service using 8-20 phr of a furnace black with a particle size in the range of N110 to N550 and 0.5 to 2.0 phr of an elastomer-type antioxidant. The minimum black required depends on its particle size and degree of dispersion. White compounds formulated for long-term outdoor service should contain at least 25 phr of a rutile TiO₂ pigment for dispersion. The above-mentioned barium-sodium organophosphate stabilizer can enhance color retention in white or pastel compounds. The incorporation of 2-4 phr of anatase TiO₂ in the pigment helps to maintain whiteness by gradual chalking of the surface.

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Service life can be very long even in full sunlight (30), but the choice of pigment, stabilizer, etc. can be critical; for optimal performance, the manufacturer should be consulted (see also COLORANTS).

Blends With Other Polymers

Little true dissolution takes place between CPE and other polymers. The miscibility with polycaprolactones, ethylene-acrylic rubbers, and a few other polymers (40-45) appears to be strongly influenced by chlorine content and distribution. More typically, a separate phase forms when CPE is combined with other polymers. Nevertheless, such compositions often have useful properties. The behavior of CPE has been compared to that of a polymeric surfactant (29) (see also COMPATIBILITY; POLYMER BLENDS).

CPE as a Modifier. The impact performance of PVC (46-49) and other polymers is enhanced by 2-20 phr CPE. At 6-8 phr, CPE increases impact resistance in rigid PVC, with only minimal loss in heat-distortion temperature or tensile strength. With increasing CPE content, the ductility of PVC increases and tensile strength, heat distortion, and flexural modulus are gradually lost. The addition of 10 phr of CPE to phthalate-plasticized PVC reduces the low temperature brittle point and the rate of plasticizer loss of a compound exposed to oil.

In polyolefins and styrene polymers, CPE preserves impact resistance in the presence of additives, eg, FR synergists (50-52). As much as 30-35% of CPE may be used to improve the impact resistance of a rigid, brittle styrene-acrylonitrile copolymer (SAN). The product appears to contain two continuous phases, CPE and SAN, and behaves like an acrylonitrile-butadiene-styrene terpolymer (ABS), but without uv sensitivity. Incorporation of CPE improves the paintability and oil resistance of polystyrenes.

Modification by Other Polymers. CPE can be blended with polyurethanes (qv) in all proportions; amounts >40% improve fusion properties. Blends with styrene-butadiene block copolymers (qv) (53) exhibit better oil resistance. CPE can be added to virtually any binary blend containing PVC (54,55), and is used for scrap reclamation (29,56-59).

CPE as a Base Polymer. Unless a CPE contains enough residual crystallinity to confer dimensional stability after processing, thermoplastic CPE compounds must be modified with a resinous or crystalline polymer, most commonly LDPE (15-20%) and PVC.

Modification with LDPE improves flow characteristics, heat stability, and melt extensibility, ie, the polyethylene serves as a plasticizer. The blend may lose dielectric sealing characteristics and response to solvent-based adhesives but show improvement to heat (hot-bar) sealing and hot-melt adhesives; stain resistance and cleanability are excellent. Such blends are being evaluated for use in maxillofacial prostheses (60,61) because of their combination of softness, inertness, durability, cleanability, and handling characteristics. Most ethylene copolymers show good compatibility with CPE. ABS and SAN may be added to CPE as resinous modifiers that are not heat sensitive; however, hydrocarbon resistance and heat aging may be reduced.

Blends with PVC are used where oil and flame resistance are important or where the final composition must be dielectrically welded or bonded with solvent cements. The addition of PVC impairs low temperature properties and creates heat-stabilization problems. Up to 20–25% PVC can be added to a soft CPE containing 42% Cl without excessive stiffening.

Many polymer combinations can be bonded to CPE in multilayer extrusions or laminations (62–66) (see also FILMS, MULTILAYER).

Elastomers

A variety of mechanisms can be used to cross-link CPE elastomers. Peroxide or free-radical vulcanization (qv) is used in many commercial applications (see Table 2). The peroxide cure creates numerous carbon–carbon bonds, which are stronger than sulfur–sulfur and carbon–sulfur cross-links, resulting in superior compression set and heat, ozone, and chemical resistance (67).

A peroxide cure system severely restricts the use of antioxidants, which deactivate free radicals and interfere with cross-linking (see also PEROXY COMPOUNDS). Little or no antioxidant is needed in CPE elastomer compounds because the polymer backbone contains no unsaturation. Acid fillers and aromatic compounds also interfere with free-radical cross-linking.

Unlike the peroxide cure system, the dimercapthiadiazole system (see Table 2) is compatible with inexpensive aromatic oils and is not sensitive to antioxidants (68–70), offering significant economic advantages compared to peroxide cure. There is, however, some loss in compression set and heat resistance. The thiadiazole system does not permit the use of acidic fillers, lead compounds, chlorinated paraffins, and zinc and epoxy compounds.

Elastomeric CPE cross-linked by electron-beam and gamma radiation is in commercial use. Such compounds do not contain thermally activated cure systems and thus allow the high temperature processing of viscous or crystalline CPE resins. The use of unsaturated monomers or coagents assists radiation curing (71,72) (see also CROSS-LINKING BY RADIATION).

Processing and Fabrication

Thermoplastics

Usually, CPE is in the form of fine, soft particles, which can absorb atmospheric moisture, organic solvent vapors, and liquids. The tendency to stick becomes worse as liquids are absorbed; an inert anticaking additive is often present. The soft CPE powder also fuses easily. Amorphous polymers can usually be bonded on a roll mill below 80°C. For good dispersion, temperatures as high as 200°C and above may be needed to blend CPE with a resinous material such as PVC or ABS. When CPE is the base polymer, the dispersion problem is reduced with a low molecular weight PVC. With a K-50 PVC, a compound containing 20% PVC in a 42% chlorine CPE can be successfully mixed below 175°C. The same compound with a K-70 PVC requires a temperature above 200°C to achieve good dispersion. The *K* value or Fikentscher *K* value indicates the molecular

Table 2. Properties

Ingredients, parts per 100
CPE CM01
magnesium
carbon black
phthalate p
Echo S ^a
Vanax 808 ^a
Trigonox 17
triethyl trim
Total parts
Specific gravity
Processing characteristics
Mooney viscosity
minimum
Mooney score
3 min
ODR ^a at 16
ODR ^a torque
Physical properties
100% modulus
200% modulus
tensile strength
elongation
hardness, Shore
tear, Die C
Compression
70 h at 10
70 h at 12
Air oven aging
tensile, %
elongation
hardness, Shore
Volume swell
ASTM Oil
ASTM Fuel

^a Ref. 63.

^b Santicizer 7

^c Thiadiazole

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^f Mooney score

^g Oscillating

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Table 2. Peroxide and Thiadiazole Curing Systems^a

	Thiadiazole cure	Peroxide cure
<i>Ingredients, phr</i>		
CPE CM01 36	100.0	100.00
magnesium oxide	10.0	10.0
carbon black	50.0	50.0
phthalate plasticizer ^b	30.0	30.0
Echo S ^c	2.5	
Vanax 808 ^d	0.8	
Trigonox 17/40 ^e		8.0
triallyl trimellitate		3.0
<i>Total parts</i>	193.3	201.0
<i>Specific gravity of mixture</i>	1.291	1.300
<i>Processing characteristics</i>		
Mooney viscosity MS ^f 1 at 121°C, minimum	21.5	21.0
Mooney scorch MS ^f at 121°C, 3 min	22.0	18.0
ODR ^g at 160°C, minimum	13.5	16.0
ODR ^g torque, N·m ^h	5.7	4.9
<i>Physical properties, cured 20 min at 160°C</i>		
100% modulus, MPa ⁱ	3.9	2.4
200% modulus, MPa ⁱ	8.5	6.4
tensile strength, MPa ⁱ	16.0	16.3
elongation at break, %	410	420
hardness, Shore A	67	59
tear, Die C, kN/m ^j	47	34
<i>Compression set, cured 30 min at 160°C</i>		
70 h at 100°C, %	25	23
70 h at 121°C, %	38	32
<i>Air oven aging, 70 h at 150°C</i>		
tensile, % change	-26	-17
elongation, % change	-82	-75
hardness, change	+28	+29
<i>Volume swell</i>		
ASTM Oil #3, 70 h at 121°C, %	45	46
ASTM Fuel C, 70 h at 24°C, %	79	90

^a Ref. 63.^b Santicizer 711.^c Thiadiazole derivative (Hercules, Inc.).^d R. T. Vanderbilt.^e Noury Chemical.^f Mooney small rotor, 1 s.^g Oscillating disk rheometer, ASTM D 2084.^h To convert N·m to lbf·in., divide by 0.113.ⁱ To convert MPa to psi, multiply by 145.^j To convert kN/m to ppi, divide by 0.175.

weight and is derived from the relative viscosity (73). The morphology of PVC-CPE blends has been studied in detail (74-78).

Pellets of ABS or SAN offer a more serious dispersion problem. Even on a laboratory scale it is necessary to fuse the resinous portion first, followed by addition of the CPE and other ingredients, or mix the compound in a Banbury

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mixer with a high load factor ($>70\%$) and a drop temperature of $200\text{--}220^\circ\text{C}$. (At the "drop" temperature, the material drops from the mixer.) Polystyrene pellets may also require this treatment. At about 190°C , polypropylene pellets slowly melt into a CPE compound; HDPE melts somewhat faster. LDPE melts into CPE even below 150°C .

Dry Blends. When adding liquids to PVC particles, heating is normally necessary for the resin to absorb the liquids. With CPE, on the other hand, the polymer is cooled to avoid caking; the liquids are added slowly to avoid lump formation. The liquids can be added in portions, and anticaking fillers between the portions.

Before addition to a CPE-PVC composition, plasticizers should be dispersed in the PVC; otherwise, they may be mostly absorbed by the CPE. Even in rigid PVC compounds containing only 2–8 phr of CPE, liquids should be added first to the PVC resin.

If a CPE-based compound is mixed in a ribbon blender, it is advantageous to add liquids slowly in spray form or by pumping through a perforated pipe extending through the blender. The temperature should be kept below 60°C by cooling if necessary; the blender is only stopped after cooling down. In a high intensity mixer, CPE compounds should be mixed at low speed. Liquids are added gradually with the mixer running, heat is not applied, and the temperature is kept below 100°C . The blender should not be stopped while the polymer is hot.

Banbury Mixing. The heat and shear available in a Banbury mixer usually succeed in homogenizing blends of CPE with other polymers. Usually, the mixer is run at a high load factor with a neutral rotor; the temperature is allowed to rise adiabatically as desired. Preblending of plasticizer may be required, especially in the presence of PVC. The required drop temperature may range from 150°C or less for a blend of CPE with powdered LDPE to 220°C or higher for CPE with a pelletized styrene polymer. If CPE (3–8 phr) is added to a rigid PVC compound as an impact modifier, the drop temperature should not exceed about 180°C , or the optimum morphology may be destroyed, with loss of impact resistance.

Extrusion. CPE, like PVC, is often processed by dry-blend extrusion (qv). A typical 60-mm extruder has a minimum L:D of 20:1 and is vented and equipped with a two-stage screw having an overall compression ratio between 3:1 and 3.5:1 with a minimum screw-flight depth of 6.35 mm. The screw is adapted for oil heating and cooling. Blends with a high CPE content are extruded with a lower temperature in the rear of the extruder to avoid excessive fusion before the vent is reached; otherwise, volatiles would be trapped in the melt and a porous extrudate would result. The screw oil temperature is usually somewhat lower than that used with PVC extrusion to avoid premature fusion, but die temperatures are between 170 and 200°C to minimize back pressure and adiabatic heating. Screen packs should only be used if absolutely necessary.

Blends of CPE compounds with PVC resin and PE powder lend themselves readily to dry-blend extrusion. PVC combinations in all proportions can be processed this way. With polyethylene powder, 20–30% can be readily dispersed, but with medium-sized PE pellets, 3% may be the maximum that can be handled. Styrene polymers to be blended and processed should not be in pellet form.

If a CPE blend with a resinous polymer, such as PVC, gives an apparently

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homogeneous extrudate that becomes harder upon reprocessing, it is likely that the resinous portion was incompletely dispersed. This may happen if the processing temperature is too low or if shear mixing is inadequate. Some blends of CPE with resinous, high melting polymers, eg, ABS or polycarbonate, may require Banbury mixing or a multiextruder arrangement where different polymeric ingredients can be fluxed before being dispersed.

Molding. Injection molding of CPE combined with other polymers succeeds best if all ingredients are precompounded. Dry blends can sometimes be molded on a screw-injection machine with a compression ratio of 3:1, a 16:1 or higher L:D ratio, and a vent to remove volatiles. Lubrication requirements for molding and for extrusion may be very different.

Elastomers

The first important step in the fabrication and processing of CPE elastomers is good dispersion in the polymer matrix. Internal mixers of the Banbury type are commonly used; the solids are added first, followed by liquids and CPE. Cooling, a load factor of 70%, and a drop temperature of 95–102°C are the conditions that produce satisfactory CPE elastomers. The product is cooled on a two-roll mill and cut into strips or pelletized for calendering, extrusion, or molding.

Most commercially available CPE polymers are fine enough to pass through a 840- μ m (20-mesh) screen. Other elastomers are usually available in bales or large particle form. The small CPE particles can be processed directly from a compound powder blend into a finished product. Twin-screw extruders have been used to process powdered CPE compounds directly into finished products without the labor- and capital-intensive mixing step.

Health and Safety Factors

Chlorinated polyethylene polymers have a very low toxicity (79); their primary hazard appears to be HCl evolution at high temperatures. CPE reportedly causes only minor eye and skin irritation. No LD₅₀ value has been determined. The toxicity does not appear to be affected by chlorine content or distribution.

FDA regulations (80) permit the use of CPE in the packaging of dry or water-based foods, including oil-in-water emulsions. It may not be used to package fatty or oily foods, including water-in-oil emulsions, except as a modifier in rigid PVC up to a concentration of 10%.

Applications

The 1985 worldwide production capacity for CPE was estimated to be above 50,000 metric tons per year. In the United States, The Dow Chemical Co. produces a variety of thermoplastic and elastomeric grades (amorphous and crystalline), under the trademark Tyrin CPE, ranging in chlorine content from 25 to 47%. In

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the FRG, Hoechst markets CPE products in the 35–42% chlorine range under the trade name Hostapren. Other CPE producers include Borsodi Vegyi Kombinat, Hungary, and Osaka Soda and Showa Denko, Japan. The distribution of Dow products is given below:

<i>Product designation</i>	<i>Application area</i>
Tyrin CPE 3615	PVC impact modification
Tyrin CPE 4213	flexible film and sheet
Tyrin CPE 3623	polymer alloys
Tyrin CM 0136	elastomers; wire and cable

Thermoplastics. The modification of rigid PVC is one of the largest single uses of CPE. About 2 phr of CPE in rigid PVC pipe improves impact resistance and ease of processing. It is used in PVC electrical conduits at 5–6 phr to improve impact and in vinyl house siding and related profiles at 7–10 phr to give high impact strength, which is retained after extended exposure to the sun. In other rigid polymer blends, CPE is used at 5–10 phr to aid fusion and dispersion and enhance impact; in some flame-retardant compounds it minimizes the effect of FR additives on impact resistance.

The ACS (acrylonitrile–CPE–styrene) terpolymers produced in Japan (81,82) are graft polymers on a CPE backbone. They resemble ABS except for low temperature impact resistance and show excellent uv resistance. Polymer blends similar to ACS have been produced by compounding 30–40% CPE into SAN (25–30% acrylonitrile); related work has been done on polymerization grafting (83,84) and grafting via metalation (85).

Highly Filled Compounds. Because of its high filler acceptance, CPE is used as base polymer in magnetic strip, conductive sheeting and moldings, and acoustical dampening materials (66). In heavily filled vinyl compounds it promotes fusion and wetting of the filler and prevents embrittlement.

Industrial Sheeting. CPE-based products demonstrate durability, uv resistance, vapor-barrier properties, and chemical and oil resistance (86–88). These properties have increased the use of CPE in products such as pond and reservoir linings, roofing membranes, and membranes for waterproofing and vapor-barrier installations.

Wire and Cable. CPE offers advantages for electrical applications, including cable jacketing and insulation (51,89–92).

Solution Applications. Soft amorphous CPE polymers containing 42% Cl or more are soluble in aromatic, chlorinated, and hydrocarbon solvents. Such solutions are used to coat tents and in vapor-barrier coatings over low temperature insulation. Combinations of CPE with other elastomeric polymers have been used in adhesive and caulking compositions.

Other applications include rubber–vinyl hose; pigment/additive masterbatch carrier; modifier for bituminous compositions; and as multilayer film compositions.

Elastomers. Hydraulic, automotive, and industrial hoses made from CPE elastomers exhibit excellent resistance to heat, ozone, oil, and chemicals. These elastomers are approved for use in wire and cable insulation and jacketing, where ignition resistance is required (see also WIRE AND CABLE COVERING).

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The flexibility and the resistance to ozone are valuable in outdoor applications. Sheetting applications include 4000-m² roof installations performing well after 10 years of maintenance-free service.

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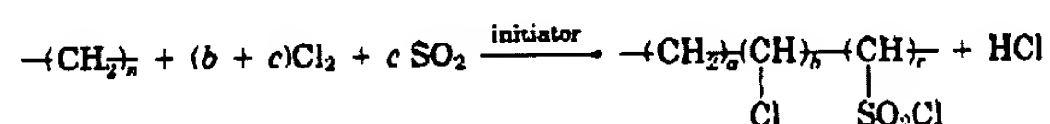
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W. L. YOUNG
 R. R. BLANCHARD
 The Dow Chemical Company

Chlorosulfonated Polyethylene

Chlorosulfonated polyethylene (CSM) is the basis of a family of synthetic elastomers prepared by the simultaneous chlorination and sulfonation of polyethylene (PE) in homogeneous solution. This reaction can be represented by



where a free-radical initiator or light is used. Because the reaction occurs in homogeneous solution, the three types of groups in the product are distributed nearly randomly along the polymer chain. In a typical elastomeric product containing 36% Cl and 1% S, they are present in the ratio $a:b:c = 108:32:1$.

The introduction of chlorine and sulfur dioxide onto the PE molecule breaks up the crystalline segments, changing a thermoplastic material into an amorphous polymer which behaves as an elastomer and can be thermoset by way of the sulfonyl chloride groups. Incorporation of chlorine also increases oil resistance. Commercial chlorosulfonated polyethylene (Hypalon) offers the advantages of superior resistance to oil, ozone, and heat compared with standard synthetic rubbers. The optimum chlorine content for an amorphous elastomer is the minimum amount required to destroy crystallinity completely. Lower chlorine content yields a material which is still partly thermoplastic, whereas higher concentrations give a product with a higher glass-transition temperature, which therefore is less rubbery but offers increased resistance to oils and nonpolar solvents. Chlorinated PE prepared in solution is very similar to CSM except that the lack of a cure site makes it more difficult to cure and allows less compounding latitude.

Preparation

The polymers described here are prepared only in homogeneous solution. The solvents must dissolve PE and CSM and be inert toward chlorinating agents. Carbon tetrachloride is usually the solvent of choice (1-3), but chlorobenzene (4,5), 1,1,2,2-tetrachloroethane (5), chloroform, trifluorochloromethane (6), methylene chloride, and mixtures thereof are also used.

Chlorobenzene is used in the laboratory since it boils sufficiently high to dissolve high density polyethylene (HDPE) at atmospheric pressure, which requires temperatures of 105-110°C. Other solvents must be used under pressure.